

Sources of Speciated Atmospheric Mercury at a Residential Neighborhood Impacted by Industrial Sources

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Speciated measurements of atmospheric mercury plumes were obtained at an industrially impacted residential area of East St. Louis, IL. These plumes were found to result in extremely high mercury concentrations at ground level that were composed of a wide distribution of mercury species. Ground level concentrations as high as 235 ng m⁻³ for elemental mercury (Hg⁰) and 38 300 pg m⁻³ for reactive mercury species (reactive gaseous (RGM) plus particulate (PHg) mercury) were measured. The highest mercury concentrations observed during the study were associated with plumes that contained high concentrations of all mercury species (Hg⁰, RGM, and PHg) and originated from a source located southwest of the sampling site. Variations in proportions of Hg⁰/RGM/PHg among plumes, with Hg⁰ dominating some plumes and RGM and/or PHg dominating others, were attributed to differences in emissions from different sources. Correlations between mercury plumes and elevated NO_x were not observed; however, a correlation between elevated SO₂ and mercury plumes was observed during some but not all plume events. Despite the presence of six coal-fired power plants within 60 km of the study site, wind direction data along with Hg/SO₂ and Hg/NO_x ratios suggest that high-concentration mercury plumes impacting the St. Louis - Midwest Particle Matter Supersite are attributable to local point sources within 5 km of the site.

Introduction

In ambient air, mercury exists predominantly as elemental mercury (Hg⁰), which is relatively inert (1-3), while the more

reactive divalent [Hg(II)] forms typically comprise less than 5% of the total amount of mercury (4-8). While Hg⁰ almost exclusively occurs in the vapor phase due to its high volatility and low solubility (2,3), Hg(II) compounds may either exist as gases (e.g., HgCl₂, HgO, Hg(OH)₂, and Hg(NO₃)₂·xH₂O) (6,8-10), which are collectively referred to as reactive gaseous mercury (RGM), or sorbed to particles (particulate mercury; PHg) (6,10). Apart from sorbed RGM forms, PHg may also incorporate condensed solid compounds such as HgO (3). Since the more reactive mercury species are represented by many of the same compounds originating from a common source, in this paper, RGM and PHg are often treated as a single entity referred to as reactive mercury (sum of RGM and PHg). While the valence state of mercury associated with particles is uncertain, Brosset and Lord (11) found that 57-85% of particulate mercury collected in Sweden was reducible by NaBH₄, and Feng et al. (12) found, using thermal release techniques, that on average 72% of particle-bound mercury collected in Toronto was composed of divalent species (HgCl₂, HgS, and HgO); accordingly, PHg has been classified as a reactive species in this work. In urban and industrial areas, reactive mercury species (RGM and PHg) may comprise more significant fractions of the atmospheric mercury pool due to the influence of anthropogenic sources (4,5,13-15), and the distribution of mercury among physical and chemical forms also may vary greatly.

Speciation plays an important role in the atmospheric cycling of mercury as it affects chemical reactivity and the removal of mercury from the atmosphere through wet and dry deposition processes (6,10,16-20). Although Hg⁰ is the dominant atmospheric mercury species, RGM is expected to dominate the total mercury depositional flux due to its higher reactivity with aerosol particles and greater water solubility (6,10). Reactive mercury species are deposited quickly (within a few hours to a few weeks) in close proximity to emission sources on a local or regional scale, whereas Hg⁰ is a global pollutant with a long residence time in the atmosphere (3,10,16,17). Predicting the environmental fate and impacts of mercury on aquatic and terrestrial ecosystems thus requires knowledge of the physical and chemical speciation of mercury. For this reason, characterization of source plumes with respect to mercury speciation is needed, but direct stack testing, while becoming more routine for well-characterized sources of mercury such as coal-fired power plants, is less common for many other sources. Additionally, mercury speciation within stack gases may not be representative of speciation downwind of the stack after dilution as reactions with other atmospheric pollutants and gas-to-particle conversion may occur (3).

The purpose of this work is to demonstrate the use of high time-resolved measurements of atmospheric mercury in combination with readily available criteria gas and meteorological measurements in understanding sources of atmospheric mercury in industrially impacted environments.

While statistical source apportionment methods, such as positive matrix factorization (PMF) and chemical mass balance (CMB) models, provide researchers and policy makers with valuable information, the application of such methods requires some subjective constraints, including the type and number of impacting sources, and may struggle to properly address less well-characterized point sources. Accordingly, the development of direct methods of assessing source contributions is warranted and is particularly attractive with regard to atmospheric mercury. Additionally, the work seeks to highlight the potential contribution of local sources of atmospheric mercury to local and regional deposition by

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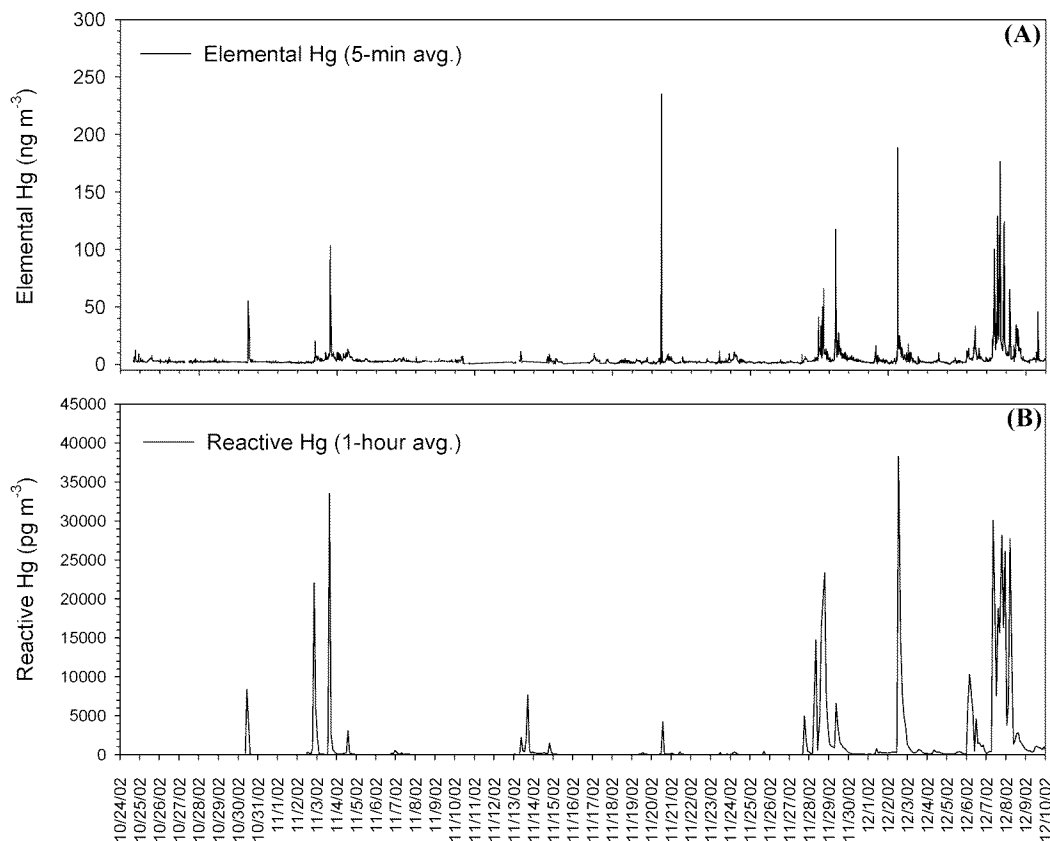


FIGURE 1. Atmospheric concentrations of (A) Hg^0 and (B) reactive mercury (sum of RGM and PHg) measured in East St. Louis, IL. Because of the possibility of a RGM breakthrough on the Tekran denuder, the concentrations of PHg and RGM during high mercury episodes may be subject to additional uncertainty.

characterizing the speciation of mercury directly downwind of industrial sources. Such an understanding is important in the light of recently emerging regulatory needs to reduce mercury emissions. To this end, atmospheric mercury species were measured semi-continuously at a receptor site situated in a residential neighborhood heavily impacted by industrial sources, using an automated mercury speciation instrument (Tekran Models 2537A, 1130, and 1135). The temporal mercury data were used with analogous meteorological data to isolate source plumes reaching the receptor site and to determine the distribution of mercury species in specific plumes. Along with wind direction data, contemporaneous measurements of SO_2 and NO_x in mercury contaminated plumes were used to elucidate likely sources of high ground level mercury concentrations impacting the receptor site.

Study Site. Concentrations of atmospheric mercury species were measured at the U.S. Environmental Protection Agency (EPA) funded St. Louis-Midwest Particle Matter Supersite from October 24 to December 10, 2002. This site is located in a residential/light commercial neighborhood approximately 3 km east of the City of St. Louis (MO) central business district. The ground level site is impacted by emissions from several point sources, many of which are located in an industrial corridor following the Mississippi River. The nearest major point sources are located in Sauget, IL, which is approximately 2 km south of the site. The Supersite operations are immediately adjacent to an Illinois EPA compliance monitoring site that includes the full suite of criteria gas monitors (SO_2 , NO/NO_x , CO , and O_3).

Materials and Methods

Atmospheric Mercury Species. A fully automated system was used to collect semi-continuous measurements of

atmospheric mercury species. The system incorporated Tekran 2537A for the determination of elemental mercury (Hg^0) and the Tekran speciation units 1130 and 1135 for the determination of RGM and fine particle (aerodynamic diameter $< 2.5 \mu\text{m}$) PHg, respectively. Thorough descriptions of the automated Tekran system and instrument components are summarized elsewhere (21, 22). The speciation unit was installed on the roof of a trailer, and samples were collected at 1.5 m above the roof. A detailed description of the operating procedures and quality control/quality assurance procedures are available in the Supporting Information.

Other Measurements. The 24 h integrated (midnight-to-midnight CST) ambient fine particulate matter samples were collected every day for more than 2 years using a battery of samplers to support various physical and chemical analyses. Relevant to this paper, $\text{PM}_{2.5}$ samples were collected on Teflon filters using Harvard impactors. The loaded filters were shipped and stored at cold conditions and were analyzed at the Desert Research Institute (Reno, NV) by X-ray fluorescence (XRF) for 40 elements including mercury (23).

Criteria gases (SO_2 and NO_x) were monitored continuously at the adjacent EPA compliance monitoring site using EPA Designated Reference or Equivalent Methods (24). Measurements at the Supersite accompanying this study also included meteorology (10 m wind speed, wind direction, and temperature; 2 m temperature and relative humidity; solar radiation; and precipitation). Additional specific QA/QC data are available in the Supporting Information (Tables S3 and S4).

Emissions Data. Emissions rate data (mercury, SO_2 , and NO_x) for point sources located within the counties surrounding the Supersite (Madison, Monroe, Randolph, and St. Clair counties in Illinois; Franklin, Jefferson, St. Charles, and St. Louis counties in Missouri; and the City of St. Louis,

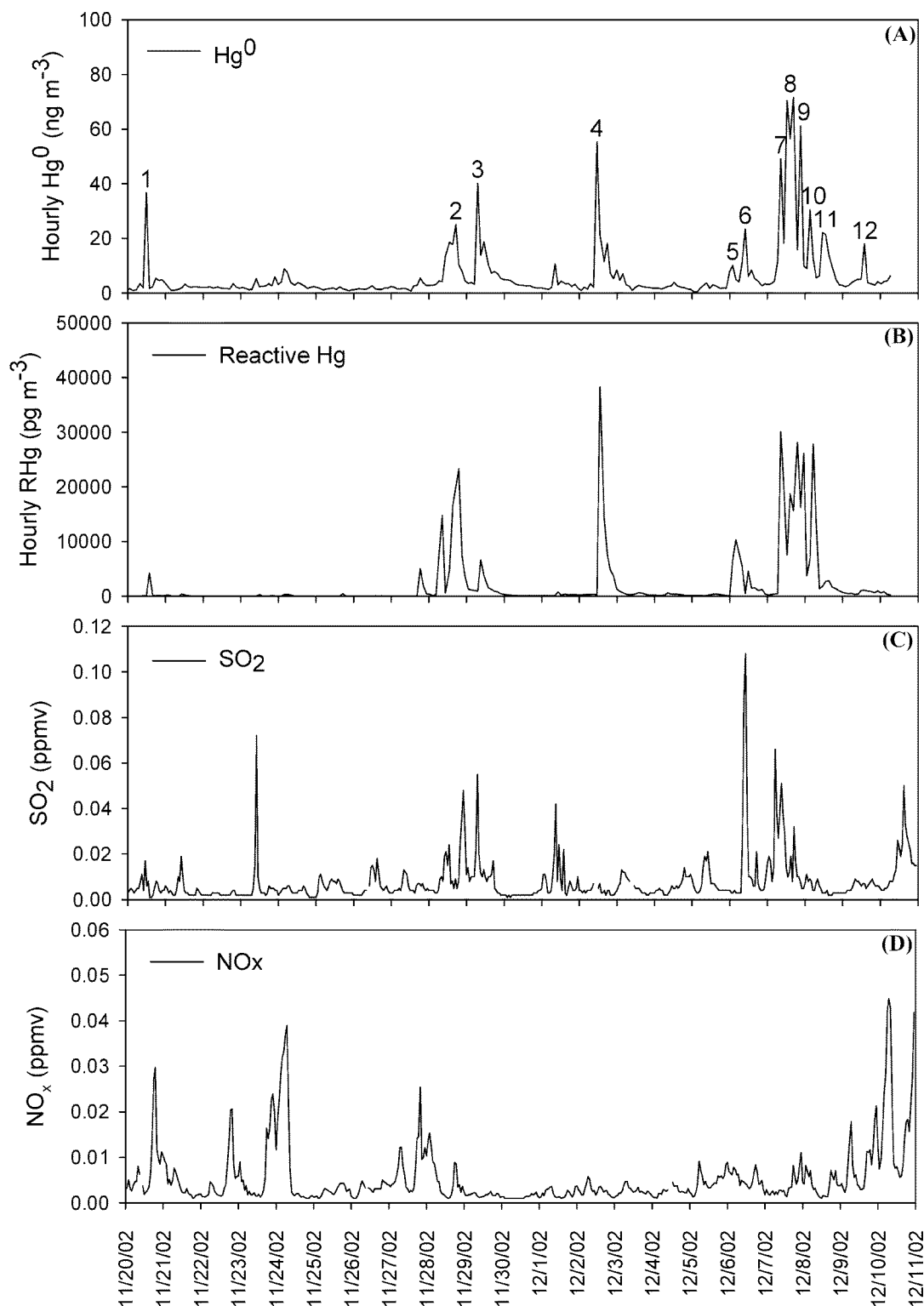


FIGURE 2. Hourly concentrations of (A) Hg^0 , (B) reactive mercury, (C) SO_2 , and (D) NO_x measured during the last 3 weeks of the sampling campaign. Distinct mercury plume events were identified and labeled on the plot (1 - 12).

MO) were obtained from the final version of the EPA's 2002 National Emissions Inventory (NEI) (25). For one of the point sources, a primary non-ferrous metals refinery, mercury emissions rate data from the EPA's Toxics Release Inventory (TRI) (26) were used in place of the NEI, which did not report any significant mercury emissions from this source. This substitution was deemed appropriate as the melting of zinc ores within this facility can be expected to result in substantial releases of mercury to the atmosphere (27, 28). Additionally, SO_2 and NO_x emissions rates for another source, a cement

kiln, were estimated using the average emissions rates for cement kilns in Missouri and Illinois taken from the 2002 NEI as data specific to this source were unavailable from the NEI.

Results and Discussion

Concentrations of Atmospheric Mercury Species. The most striking and surprising aspect of the East St. Louis data set was the exceedingly high concentrations of all atmospheric mercury species that were repeatedly measured at the ground

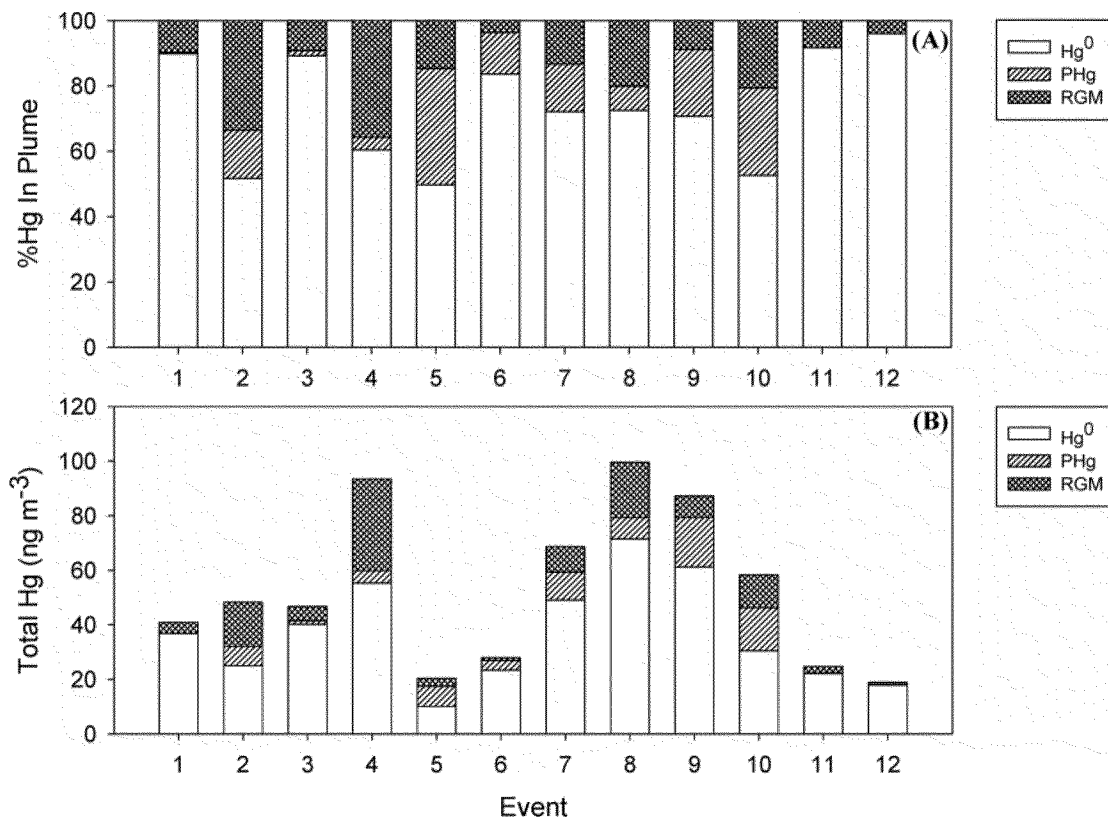


FIGURE 3. Distribution of mercury species in plume events 1–12 (shown in Figure 2) as a function of (A) percent and (B) concentration of each species present in the plumes.

level supersited during the sampling campaign. The magnitude and frequency of these extreme mercury events is illustrated in Figure 1, where 5 min integrated Hg^0 and 1 h composite reactive mercury (sum of RGM and PHg) concentrations, obtained every other hour during the sampling campaign, were plotted against time. Concentrations of Hg^0 frequently ranged between 50 and 200 ng m^{-3} and reactive mercury between 5000 and $35\,000 \text{ pg m}^{-3}$. Maximum Hg^0 and reactive mercury concentrations of 235 ng m^{-3} and $38\,300 \text{ pg m}^{-3}$, respectively, were measured during this period. These concentrations are at least 2 orders of magnitude higher than ambient levels [background levels in North America of $\uparrow 3 \text{ ng m}^{-3}$ for Hg^0 (16); $50\text{--}200 \text{ pg m}^{-3}$ for RGM (6, 8); and $<90 \text{ pg m}^{-3}$ for PHg (5, 7, 29)]. When the Supersite was not being impacted by highly contaminated mercury plumes, concentrations of all mercury species often dropped to background levels.

Atmospheric mercury concentrations of similar magnitude only have been reported for measurements taken at or in very close proximity to point sources. Landis et al. (30) reported respective concentrations for gaseous elemental mercury (Hg^0) and RGM of 186.1 ng m^{-3} (5 min average) and 9 pg m^{-3} (2 h average) within 1 km downwind of a chlor-alkali plant, while concentrations of both species reached microgram per cubic meter levels inside the plant. Tan et al. (14) measured TGM and RGM concentrations as high as 1100 (192 and 146) (15 ng m^{-3} , respectively, at a mercury refining workshop in Guizhou Province, China, while concentrations measured at several urban centers throughout Guizhou influenced by coal combustion sources ranged from 9 to 12 ng m^{-3} for TGM and from 0.80 to 1.46 ng m^{-3} for RGM. RGM composed 15% of the TGM at the refinery and 13% of the TGM at the urban centers. Within 5 km of a coal combustion source in Guiyang, China, Feng et al. (31) reported TGM and RGM concentrations of 70 ng m^{-3} (5 min average) and 739 pg m^{-3} (24 h average), respectively. Average PHg values reported in the literature for urban areas range from 26 pg m^{-3}

in St. Anicent, Quebec (32), to 19.8 pg m^{-3} for Detroit, MI (5), to 16.4 pg m^{-3} for Tuscaloosa, AL (33).

Although impressively high, $38\,300 \text{ pg m}^{-3}$ represents a conservative estimate of the maximum reactive mercury concentration measured at East St. Louis. Since reactive mercury concentrations were much greater than anticipated, the linear range of the 2537A analyzer (refer to Supporting Information Figure S1) was often exceeded within a 1 h sampling period. Consequently, accurate quantification of RGM and PHg at these extremely high concentrations was not possible, and concentrations greater than $\uparrow 12\,000 \text{ pg m}^{-3}$ were underestimated by as much as 20% in the case of $38\,300 \text{ pg m}^{-3}$. X-ray fluorescence (XRF) analysis conducted on 24 h integrated $\text{PM}_{2.5}$ (particulate matter with an aerodynamic diameter $<2.5 \mu\text{m}$) samples that were collected daily from mid-April, 2001 through June, 2003 (refer to Figure S2 for a sample of the data set) confirmed the occurrence of exceedingly high PHg concentrations at the Supersite. The 24 h integrated PHg concentrations determined through XRF were found to be generally higher (e.g., maximum of $61\,500 \text{ pg m}^{-3}$) than analogous 24 h averages determined through the Tekran 1135 (average of corresponding 1 h measurements). The higher concentrations may have been a combined result of artifacts due to adsorption of RGM onto the $\text{PM}_{2.5}$ filter (XRF), which did not include a denuder in the sample train, extremely high PHg concentrations being underestimated by the Tekran 2537A analyzer, and the full extent of the mercury plume being missed during sampling by the Tekran as sampling was interrupted every other hour for analysis.

Sources of Atmospheric Mercury. Data collected during the sampling campaign (Figure 1) were investigated further to characterize high-concentration mercury plumes impacting the Supersite and to broadly identify their respective sources. At least 12 high-concentration mercury plumes were observed at the Supersite during the 7 week period extending from November 20 to December 10, 2002. Clusters of peaks

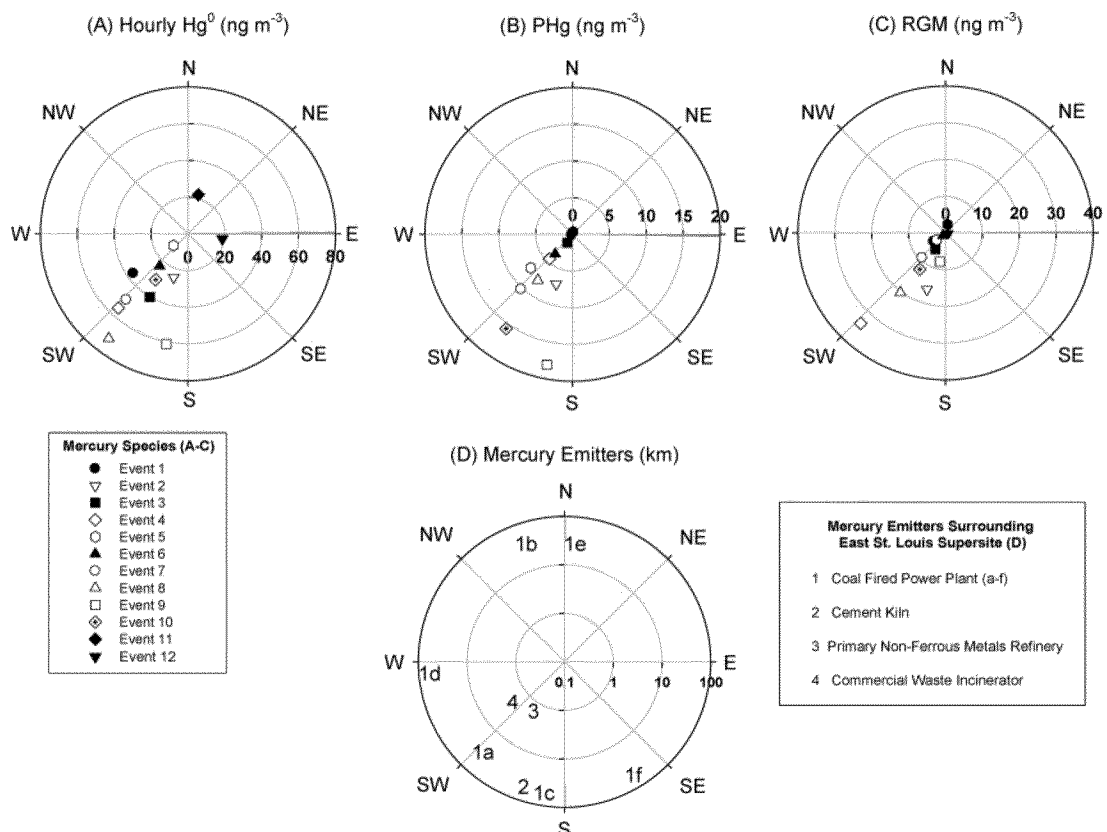


FIGURE 4. Hourly concentrations of (A) Hg^0 , (B) RGM, and (C) PHg measured in plume events 1 - 12 shown in Figure 2, plotted against wind direction. The center of each polar plot represents the St. Louis - Midwest Particle Matter Supersite, and the relative locations of known mercury emitting industries reporting to the U.S. EPA Toxics Release Inventory (TRI) are shown in panel D.

representing distinct plumes were identified and were labeled (1 - 12) on the time series plot shown in Figure 2a. Plumes were primarily identified based on time of occurrence and wind direction; however, speciation was used to differentiate plumes that occurred sequentially, particularly when speciation in such plumes differed significantly from one another. Hourly Hg^0 and reactive mercury concentrations are shown in Figure 2a,b, respectively, and hourly concentrations of SO_2 and NO_x for the same period in Figures 2c,d, respectively. The mercury speciation of each peak was determined by calculating the percentage of the total mercury concentration (sum of the three species) as Hg^0 , RGM, and PHg (Figure 3a). The distribution and concentration of each mercury species within each peak shown in Figure 3b, along with concurrent measurements of wind direction, SO_2 , and NO_x , are summarized in the Supporting Information (Table S1).

It is apparent from the polar plots shown in Figure 4a - c that the most significant sources of mercury contaminated plumes that impacted the Supersite during the 7 week period were located southwest of the site, with a few significant Hg^0 sources also situated to the north, west, and southeast. Mercury contaminated plumes most frequently originated from the southwest direction and typically contained the highest observed concentrations of all mercury species. These observations were generally true for all high-concentration mercury, as well as sulfur dioxide, plumes that were measured at the Supersite throughout the sampling campaign and are consistent with the spatial distribution of the major industrial zones in the area; the area west of the Supersite is primarily the St. Louis city center, and areas surrounding the city center are urban/suburban residential regions with relatively fewer point sources.

Trends in mercury speciation were observed among the clusters with Hg^0 dominating some plumes and RGM and/or PHg others. Hg^0 comprised 80 - 95% of the total amount

of mercury in plumes represented with solid symbols in Figure 4a - c. Apart from containing low fractions of reactive mercury species, these plumes also contained among the lowest concentrations of RGM and PHg (Figure 4b,c and Table S1). For example, plumes denoted with solid symbols (Figure 4a - c) originating north and east of the Supersite where significant sources of reactive mercury were not observed contained relative fractions of $\text{Hg}^0/\text{RGM}/\text{PHg}$ of 90:10: <1 and RGM and PHg concentrations of <2400 and <15 pg m⁻³, respectively. Because of exceedingly high concentrations of RGM and/or PHg, reactive mercury species comprised more significant fractions (20 - 60%) of the total amount of mercury in plumes represented with white symbols in Figure 4a - c, even though Hg^0 concentrations in these plumes often exceeded 50 ng m⁻³. The mercury speciation varied widely among these plumes with Hg^0 fractions ranging from 20 to 70%, RGM from 20 to 40%, and PHg from 20 to 60%.

Several mercury emitting industries are situated within a 100 km radius of the Supersite, and the relative locations of facilities whose stack mercury emissions exceed 20 lbs/year according to the 2002 NEI/TRI (25, 26) are shown in Figure 4d. Located directly southwest of the Supersite, the same direction from which the most significant mercury plumes originated, are a primary nonferrous metals refinery and a commercial refuse incinerator at 1.6 and 2.2 km, respectively. A coal-fired power plant is also located in the same direction at 54.2 km as is a cement kiln at 50.6 km. Five other coal-fired power plants are located 30 - 60 km north, west, south, and southeast of the Supersite (Figure 4d). However, it should be noted that despite the presence of numerous sources of mercury in and around the St. Louis metropolitan area, the six coal-fired power plants located in the area are, by far, the most significant sources of both

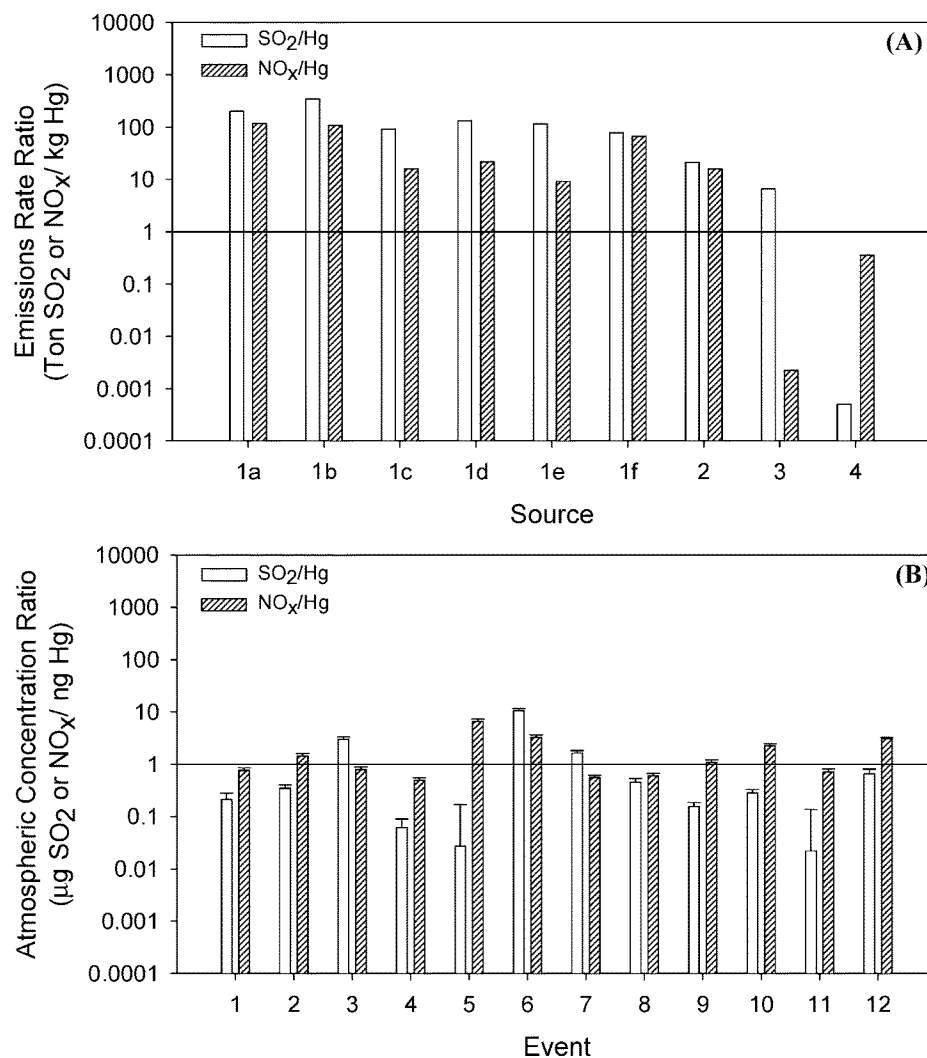


FIGURE 5. NO_x/Hg and SO₂/Hg emissions rate ratios for known mercury emitters surrounding the St. Louis - Midwest Supersite (A) as compared to the atmospheric concentration ratios of NO_x/Hg and SO₂/Hg of mercury contaminated plumes observed at the site (B).

elemental and reactive mercury according to the NEI/TRI (Figure S3).

SO₂, NO_x, Hg⁰, and Hg²⁺ have all been identified as significant constituents of coal combustion emissions and are typically co-emitted from coal-fired plants (e.g. refs 16, 34, and 35). According to the 2002 NEI, significant quantities of SO₂ and NO_x are emitted from each of the coal-fired power plants surrounding the Supersite and from the remaining (non-power plant) sources of mercury identified by the NEI (25). Consequently, trends between observed concentrations of mercury species and SO₂ and NO_x might be expected, and such trends might prove useful in elucidating the source(s) of mercury contaminated plumes impacting the site. Hourly measurements of SO₂ and NO_x collected concurrently with mercury data at the Supersite are shown in Figure 2c,d. Elevated concentrations of SO₂ relative to background levels were often observed during the passing of mercury contaminated plumes containing high concentrations of reactive mercury and/or Hg⁰, but the pattern was not consistent. A less discernible pattern was observed with NO_x. Furthermore, it was noticed that as with mercury contaminated plumes, the most significant SO₂ contaminated plumes originated only from the southwest direction. One coal-fired power plant is located in this direction; however, several others are situated in other directions from which mercury and SO₂ contaminated plumes were not detected (Figure 4d).

The sheer magnitude of the ground level mercury concentrations observed during plume events would seem

to preclude their originating from distant sources, such as the power plant or cement kiln located ~50 km southwest of the Supersite, as significant dilution of mercury concentrations in plumes emanating from these sources might be expected prior to reaching the site. However, as a check on this hypothesis, the atmospheric concentration ratios of SO₂/Hg and NO_x/Hg were determined for each of the plumes identified in Figure 2a and compared with the emissions rate ratios for each of the mercury sources identified in the NEI. As shown in Figure 5A, the emissions from the power plants surrounding the Supersite (sources 1a-f) as well as the cement kiln (source 2) are highly enriched in the SO₂ and NO_x as compared to mercury. By contrast, the emissions from the primary non-ferrous metals refinery (source 3) and the commercial waste incinerator (source 4) have much lower SO₂/Hg and NO_x/Hg emissions ratios. Additionally, it should be noted that the SO₂/Hg ratio ascribed to the metals refinery may be an overestimation as, while SO₂ may be emitted in significant quantities during smelting, considerable amounts of SO₂ are also released from this facility during the production of sulfuric acid, which may not take place concurrently with smelting operations.

Emissions inventory data used to calculate NO_x/Hg and SO₂/Hg ratios represent an annual average and may not be representative of daily emissions throughout the year. For example, some NO_x emissions controls, such as selective catalytic reduction (SCR), might be turned off during the winter months for many power plants, which can affect the

NO_x/Hg ratio. If the power plant NO_x/Hg ratios were higher during the December study period than indicated in Figure 4A, this would reinforce our conclusions that the local point sources are driving the observed Hg high concentrations.

As shown in Figure 5b, the atmospheric concentration ratios of SO₂/Hg and NO_x/Hg observed during all 12 plume events do not demonstrate the level of enrichment of SO₂ or NO_x as compared to Hg that would be expected if the source of these plumes were either one of the coal-fired power plants or the cement kiln. Although it might be argued that the emissions ratios from these sources may not be conserved during transport, the SO₂/Hg and NO_x/Hg ratios in these source plumes are, on average, 2 orders of magnitude greater than the observed atmospheric concentration ratios. It is unlikely that SO₂ or NO_x would be preferentially lost during transport to an extent that would produce the atmospheric concentration ratios observed at the Supersite. Instead, it is more likely that the sources of mercury contaminated plumes impacting the site are the more proximate ones, the primary non-ferrous metals refinery and the commercial waste incinerator located within 2 km of the site, and not the coal-fired power plants or the cement kiln. This conclusion is supported by both the magnitude of the mercury concentrations observed as well as the trends between observed concentrations of mercury species and SO₂ and NO_x. It is worth noting that the sources implicated here have low stack heights (less than 50 m) and accordingly can impact ground level mercury concentrations very close to the stack. This conclusion was supported using Gaussian plume model over all stability classes. These models consistently showed that plumes from both sources would significantly impact the study site.

These results demonstrate the efficacy of high time-resolved measurements of mercury coupled with readily available criteria gas and meteorological measurements to directly assess the contribution of less well-characterized sources of atmospheric mercury. Additionally, such methods are ideal in assessing the relative impact of such sources on mercury deposition in comparison to coal combustion and long-term transport.

Acknowledgments

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Supporting Information Available

Complete plume event data set including Hg speciation and SO₂/NO_x concentrations, Tekran calibration curve showing the linear range of the CVAFS detector, time series of PHG concentrations determined by XRF, and TRI mercury emissions by source category. Additional QA/QC information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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